Effects of Ion Association on Rates of Substitution in *trans*-$[Ir(en)_2Cl_2]^+$ in Mixed Aqueous Solvents

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The rate of ligand substitution reaction in *trans*-$[Ir(en)_2Cl_2]^+$ by Cl^-, Br^-, and NO_2^- has been investigated in water, water–dioxan, and water–ethanol (up to 60% v/v dioxan or ethanol). The effects of variation of ligand, ion concentration, solvent, and temperature are discussed. The results show ion-pair formation in all of the cases studied.

THIS paper is an extension of the previous work on isotopic exchange reactions in *trans*-$[Ir(en)_2Cl_2]Cl$ in aqueous solution,[1] both to mixed aqueous solvents and to substitution with net chemical change. The previous paper [1] reported isotopic exchange in related complexes. We have now studied ligand substitution reactions in aqueous and non-aqueous solution to see if ion pairing could be detected kinetically in these cases. By use of mixed aqueous solvents the variation of rate constant with Grunwald–Winstein solvent Y values [2] may be studied and hence information obtained about the mechanism. For aquation of the closely related complex *cis*-$[Co(en)_2Cl_2]^+$, correlation of rate constants with solvent Y values has recently been described.[3]

There have been both preparative [4] and kinetic [5] studies of ligand substitution in *cis*- and *trans*-$[Ir(en)_2Cl_2]^+$. Bauer and Basolo [5] found that the rate of ligand substitution in *trans*-$[Ir(en)_2Cl_2]^+$ in aqueous solution is independent of the nature and concentration of the incoming nucleophile. We have found that under rather different conditions, at lower temperatures, ion pairing becomes significant and the rate of the reaction depends both on the nature and the concentration of the incoming nucleophile (Cl^-, NO_2^-, Br^-, and I^-).

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[2] E. Grunwald and S. Winstein, *J. Amer. Chem. Soc.*, 1948, **70**, 846.

[3] J. Burgess, *J. Chem. Soc.* (*A*), 1970, 2073.

[4] I. B. Baranovskii, G. S. Kovalenko, and A. V. Babaeva, *Russ. J. Inorg. Chem.*, 1968, **13**, 1708.

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EXPERIMENTAL

The complex *trans*-[Ir(en)$_2$Cl$_2$]ClO$_4$ was prepared by the method of Bauer and Basolo.[6] The product was then converted into the chloride by passage through De-Acidite FF X8 (100—200) in the chloride form. The complex *trans*-[Ir(en)$_2$Cl$_2$]Cl was labelled internally by equilibration with 50 μCi H^{36}Cl at 90 °C for 2 weeks. The solution was then passed through De-Acidite FF X8 (100—200) in the bromide or nitrite form. Electrophoresis of a sample of the product showed that there was no active anionic chloride outside the complex. The solution was evaporated *in vacuo* and the solid was stored in a desiccator.

The kinetic runs were carried out by taking an accurate weight of *trans*-[Ir(en)$_2$Cl$_2$]$^+$X ($X = Cl^-$, Br^-, or NO_2^-) to make a $5{\cdot}0 \times 10^{-3}$M-solution, which was transferred into a standard flask and the volume was made up with water and/or dioxan (Scintillation grade) or ethanol according to the desired volume percentage of the mixed solvent.

In the case of isotopic exchange the results were treated as reported in the previous paper.[1]

The rate of ligand substitution reactions was followed by radiochemical techniques similar to the previous work.[1] For ligand substitution the values of $\log\left(\frac{a-x}{a}\right)$ were plotted against time t, where a is the initial activity of the complex, $a - x$ is the remaining activity. All data were processed on a Honeywell series 200 computer using a least-squares programme, the rate constant with its standard deviation was obtained from the gradient.

RESULTS AND DISCUSSION

The dependence of the rate constant on the concentration of chloride, bromide, and nitrite is shown in Figures 1 and 2. In all the substitution reactions studied the rate constant varies with incoming ligand concentration. It reaches a constant limiting value, for example, at bromide concentrations greater than 0·2M. This behaviour is similar to the trends observed in *cis*-[Co(en)$_2$Cl$_2$]$^+$ in methanol,[7] *trans*-[Rh(en)$_2$Cl$_2$]$^+$ in water and water–dioxan mixtures,[8] and *trans*-[Ir(en)$_2$Cl$_2$]$^+$ in aqueous solution.[1] As the Cl$^-$, Br$^-$, or NO$_2^-$ ion concentration increases, more ion pairs are formed by the rapidly established pre-equilibrium (1).

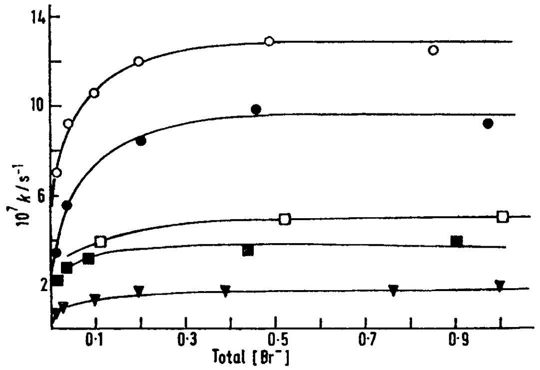

FIGURE 1 Rates of substitution in *trans*-[Ir(en)$_2$Cl$_2$]$^+$ as a function of bromide concentration at 90 °C in: ○ aqueous solution; ● 20% v/v dioxan; □ 40% v/v dioxan; ■ 60% v/v dioxan; ▼ 60% v/v dioxan and at 80 °C

$$trans\text{-}[\mathrm{Ir(en)_2Cl_2}]^+ + X^- \underset{}{\overset{K_{\mathrm{IP}}}{\rightleftharpoons}} trans\text{-}[\mathrm{Ir(en)_2Cl_2}]^+, X^- \quad (1)$$

This can be followed either by rate-determining ligand interchange (2) within the ion pair, or by dissociative

$$trans\text{-}[\mathrm{Ir(en)_2Cl_2}]^+, X^- \xrightarrow{k_{\mathrm{IP}}} trans\text{-}[\mathrm{Ir(en)_2XCl}]^+, \mathrm{Cl}^- \quad (2)$$

interchange with water from the primary solvation shell and subsequent conversion of the aquo- to the chloro-, bromo-, or nitro-complex.[5] It is not possible to distinguish between these alternatives on the basis of the available kinetic results.

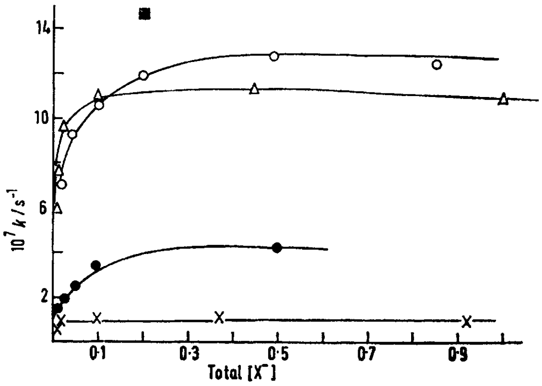

FIGURE 2 Rates of substitution in *trans*-[Ir(en)$_2$Cl$_2$]$^+$ as a function of incoming ligand concentration at 90 °C in aqueous solution: ● chloride; ○ bromide; ■ iodide; △ nitrite; × chloride in 20% dioxan

The rate law is

$$-\mathrm{d}[trans\text{-}\mathrm{Ir(en)_2Cl_2}^+]/\mathrm{d}t = k_{\mathrm{obs}}[trans\text{-}\mathrm{Ir(en)_2Cl_2}^+]$$

$$k_{\mathrm{obs}} = \frac{k + k_{\mathrm{IP}}K_{\mathrm{IP}}[X^-]}{1 + K_{\mathrm{IP}}[X^-]} \quad (3)$$

where k is the rate constant for reaction of the free ion, k_{IP} that for reaction of the ion-pair, and K_{IP} the equilibrium constant for ion-pair formation [equation (1)]. From this equation and the rates reported in Tables 1, 5, and 6 one can estimate K_{IP} from plots of k_{obs}^{-1} *vs.* $[X^-]^{-1}$ as shown in Figure 3 and Table 4.[9]

Table 4 shows that the values of K_{IP} increase in the order $Cl^- < Br^- < NO_2^-$. This might be expected, as the softer anions could lead to higher ion-pair formation.

It would be expected that more ion-pair formation should occur in less polar solvents than water and hence higher values of ion-pair equilibrium constant, K_{IP}, should be observed. However, the experimental

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[6] R. A. Bauer and F. Basolo, *Inorg. Chem.*, 1969, **8**, 2231.

[7] M. L. Tobe, ' Mechanisms of Inorganic Reactions,' Advances in Chemistry Series 49, 1965.

[8] F. M. Mekhail, unpublished results.

[9] B. Bosnich, C. K. Ingold, and M. L. Tobe, *J. Chem. Soc.*, 1965, 4074.

TABLE 1

Variation in rate constant with bromide concentration at different temperatures and solvent compositions

% Nonaqueous component (v/v dioxan)	Temp./°C	$[\mathrm{Br}^-]/\mathrm{M}$	$10^7k/\mathrm{s}^{-1}$
0	90	0·0168	7·0 ± 0·2
		0·0486	9·2 ± 0·2
		0·1084	10·6 ± 0·3
		0·202	11·9 ± 0·3
		0·493	12·9 ± 0·3
		0·856	12·5 ± 0·2
20	90	0·01378	3·4 ± 0·2
		0·0478	5·5 ± 0·4
		0·0996	9·5 ± 0·2
		0·4639	9·8 ± 0·1
		0·971	9·1 ± 0·2
40	90	0·112	3·9 ± 0·1
		0·523	4·9 ± 0·2
		1·007	4·9 ± 0·01
60	90	0·0174	2·2 ± 0·2
		0·038	2·7 ± 0·1
		0·085	3·1 ± 0·1
		0·442	3·7 ± 0·2
		0·9007	3·9 ± 0·2
60	80	0·0163	0·7 ± 0·1
		0·0210	0·8 ± 0·1
		0·1059	1·2 ± 0·1
		0·204	1·3 ± 0·2
		0·399	1·6 ± 0·3
		0·762	1·6 ± 0·4
		1·004	1·8 ± 0·1

TABLE 2

Variation of rate constant with temperature in 60% v/v dioxan

Temp./°C	$10^7k/\mathrm{s}^{-1}$
76·5	0·6 ± 0·1
80·0	0·7 ± 0·2
85·3	1·8 ± 0·1
90·2	2·4 ± 0·2
96·4	4·7 ± 0·3

TABLE 3

Rate constants as a function of Y values at 90 °C

% Nonaqueous component (v/v)		Y	$10^7k/\mathrm{s}^{-1}$
0		3·493	12·5
20	dioxan	2·877	9·5
40		1·945	5·0
60		0·715	3·5
20	ethanol	3·051	9·3
60		1·124	5·6

TABLE 4

Ion association constants and limiting rates for isotopic and substitution reactions of *trans*-$[\mathrm{Ir(en)_2Cl_2}]^+$ in water at 90 °C

X^-	$10^7k/\mathrm{s}^{-1}$	K_{IP}
Cl^-	4·3	28
Br^-	12·6	80
$\mathrm{NO_2}^-$	11·2	207
I^-	14·5 *	

* From Bauer and Basolo, ref. 5.

conditions cannot be extended to much lower concentrations of the incoming ligand, which prevents adequate estimation of the K_{IP} values.

Although Bauer and Basolo [5] have not reported the ion-pair effect in *trans*-$[\mathrm{Ir(en)_2Cl_2}]^+$ in aqueous solution at 130 °C, there is evidence for ion-pairing involving $[\mathrm{M(en)_2Cl_2}]^+$ ($\mathrm{M = Co^{III}, Rh^{III}, Ir^{III}}$) in mixed aqueous solutions [7,8] and in aqueous solution at lower temperatures.[1] At the higher temperature, 130°, ion-pair formation is less likely to occur due to the increase in the thermal energy of the solvent. Also Bauer and Basolo [5] did not study the substitution reaction in *trans*-$[\mathrm{Ir(en)_2Cl_2}]^+$ at low enough concentrations of the incoming nucleophile for observation of the kinetic

TABLE 5

Isotopic exchange data in water, at 90 °C

% Dioxan	$[\mathrm{Cl}^-]/\mathrm{M}$	$10^7k/\mathrm{s}^{-1}$
0	0·017	1·5 ± 0·1
	0·027	1·9 ± 0·1
	0·0525	2·5 ± 0·2
	0·100	2·2 ± 0·2
	0·500	4·2 ± 0·1
20	0·012	0·55 ± 0·12
	0·016	0·65 ± 0·14
	0·102	0·90 ± 0·12
	0·37	1·00 ± 0·13
	0·925	0·98 ± 0·13

TABLE 6

Rate contants of substitution reactions of *trans*-$[\mathrm{Ir(en)_2Cl_2}]^+$ in water at 90 °C

$[\mathrm{NO_2}^-]/\mathrm{M}$	$10^7k/\mathrm{s}^{-1}$
0·006	5·9 ± 0·2
0·010	7·7 ± 0·1
0·024	9·6 ± 0·3
0·105	10·9 ± 0·4
0·445	11·3 ± 0·2
1·00	10·9 ± 0·1

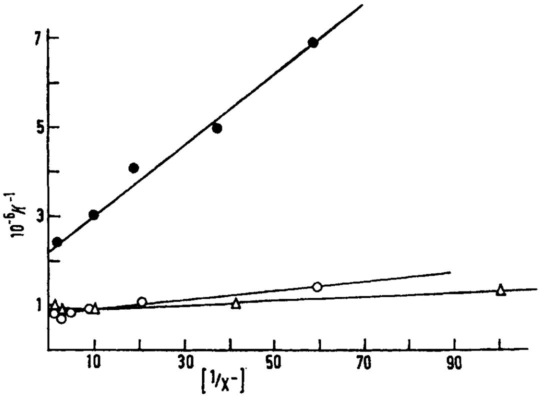

FIGURE 3 Plot of k_{obs}^{-1} *vs* $[\mathrm{X}^-]^{-1}$ in *trans*-$[\mathrm{Ir(en)_2Cl_2}]^+$: ● chloride; ○ bromide; △ nitrite

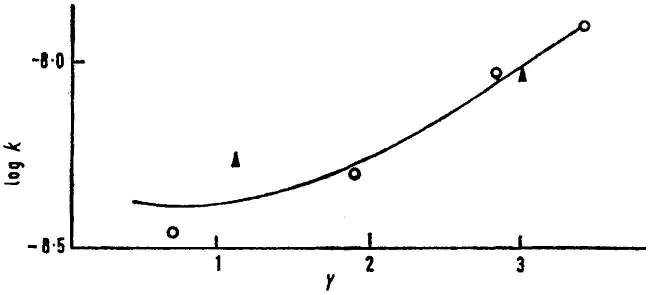

FIGURE 4 Correlation of the logarithms of the rate constant for the substitution of *trans*-$[\mathrm{Ir(en)_2Cl_2}]^+$ in mixed aqueous solvents with solvent Y values. Nonaqueous component: ○ dioxan; ▲ ethanol

consequences arising from ion-pairing equilibria with association constants of the order of magnitude suggested in the present paper.

The variation of rate constant, for *trans*-$[Ir(en)_2Cl_2]^+$ in aqueous solution and at 90°, with the nature of the incoming nucleophile is also shown in Table 4. The rate increases in the following order $Cl^- < NO_2^- < Br^- < I^-$. The rate constant for I^-, $14{\cdot}5 \times 10^{-7}$ s^{-1}, was derived by interpolation of the Bauer and Basolo results at 0·2M iodide concentration. This increase in rate constant (k_{IP}) from Cl^- to I^- is the opposite trend to the one expected for an S_N2 process.[10] It seems that the size of the hydrated nucleophile plays an important role in the substitution reaction. The less hydrated the anion (I^-) then the easier the nucleophilic attack to the central metal ion. This indicates that the reaction may proceed by a dissociative mechanism. However, the unexpectedly low rate of nitrite ion substitution, may be due to steric hindrance in the interchange process due to the large size of the NO_2^- ion.

The effect of the temperature on the substitution reactions is shown in Figure 1, where the effects of variation of solvent composition and of temperature are illustrated. Table 2 shows the variation of the rate constant with temperature in 60% dioxan and for bromide concentration of 0·015M. Values of log *k* were plotted against reciprocal of absolute temperature. From the slope of the straight line the activation enthalpy $\Delta H^{\ddagger}$ for the substitution reaction was found to be $26{\cdot}5 \pm 1{\cdot}5$ kcal mol^{-1} and $\Delta S^{\ddagger} = -16 \pm 5$ e.u.

The effect of solvent variation on the rate of the substitution at 90 °C is shown in Figure 2 which is a plot of log *k* against *Y* values of the mixed solvent; *Y* represents the solvating power of the solvent.[11] In water-rich solvents (0—30% non-aqueous component) the plot approximates to a straight line with slope (*m*) 0·25. The values of *Y* were taken from ref. 11 and at 25 °C.

The *m* value of 0·25 is consistent with the corresponding value for the aquation of *trans*-$[Co(en)_2Cl_2]^+$ [12] and similar to *cis*-$[Co(en)_2Cl_2]^+$, $m = 0{\cdot}35$ (ref. 3) at 35 °C. The value of *m* obviously depends on temperature but the variation, at least for organic substrates, is relatively small.[2] This result is consistent with a dissociative mechanism with (as solvation of the leaving chloride will be a constant factor) the solvation requirements of the $Ir(en)_2Cl$ moiety very similar to those of the $Co(en)_2Cl$ moiety.

[1/1918 *Received, 15th, March* 1971]

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